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HALL EFFECT IN EVAPORATED FILMS OF IRON, NICKEL, COBALT, PALLADIUM AND PLATINUM.

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HALL EFFECT IN EVAPORATED FILMS OF IRON, COBALT, NICKEL, PALLADIUM, AND PLATINUM

By H. B. Peacock

Abstract

Hall coefficients of evaporated films.—The Hall coefficients for films of Fe, Co, Ni, Pd, and Pt, 6 to 270$\mu\mu$ thick, deposited on surfaces at a distance less than the mean free path from the evaporating filament, were measured. For films of the ferromagnetic metals, Fe, Co, Ni, the Hall coefficients were respectively 1.4, 4.9, and 7.8 times the values for the corresponding metals in bulk, these factors being in the order of the atomic numbers of the elements. For the paramagnetic, negative Hall effect metals, Pd and Pt, the Hall coefficients were 0.66 and 0.64 times the values for the metals in bulk. The increased Hall effect for the films of the ferromagnetic metals seems closely related to ferromagnetism, although Ni, the least ferromagnetic of the three, shows the greatest variation. Films of Ir and Rh, formed at a distance less than the mean free path from the evaporating filament, showed for Ir a positive Hall effect as in bulk, and for Rh no detectable effect.

Specific resistance of evaporated films.—The ratios of the specific resistances of the evaporated films to the specific resistances of the corresponding metals in bulk were found to be 3.1 (Fe), 23.0 (Co), 25.0 (Ni), 4.4 (Pd), 14.0 (Pt), 10.8 (Ir), 12.0 (Rh).

Saturation of the Hall e.m.f.—Curves show that the saturation of the Hall e.m.f. occurs for evaporated Fe at a slightly lower magnetic induction than for Fe in bulk; for Co, at about 12,500 gauss as compared with 13,500 for bulk; and for Ni, at about 2500-3000 as compared with 6000 for bulk. It is significant that the magnitudes of these variations from bulk values, like the corresponding variations in the Hall coefficient, occur in the order of these elements in the periodic table.

Effects of Heating.—Heating films of the ferromagnetic metals during or after deposition decreased the Hall coefficients and specific resistances to approximately the values for the metals in bulk. It also caused a shift in the value of the magnetic induction necessary to produce saturation of the Hall e.m.f. toward that for the metals in bulk. No effect of heating was observed in the paramagnetic metals.

Interpretation.—Evaporated films may differ from bulk metal in the size of the crystalline grains, in the nature of the material between them or in an asymmetry of the crystalline grains which may be an important factor in the causes of the Hall effect.

Introduction

Steinberg[1] has shown that for evaporated films of the diamagnetic, negative Hall effect metals, silver and copper, the Hall coefficients were smaller than for the same metals in bulk, while for iron, which shows a positive Hall effect, this coefficient was considerably larger than the

[1] J. C. Steinberg, Phys. Rev. **21**, 22 (1923).

bulk value. Also, for evaporated films of iron, the magnetic induction necessary to produce saturation of the Hall e.m.f. was about half as large as is required for bulk iron. For all of these metals, the Hall coefficients were found to be independent of the thickness. He found the specific resistance of these films to be much larger than for the massive metals, which is in agreement with the work of Weber and Oosterhuis,[2] and also observed the usual critical thickness. He believed the Hall effect to be practically independent of the structure except as it affects the magnetic condition of the crystals. The work of Sorenson[3] shows that the magnetic properties of evaporated ferromagnetic films are different from massive metals but no suggestion is offered as to the cause underlying the results observed by Steinberg on iron.

The present study repeats Steinberg's work on iron and extends the investigation to some other metals of the same group in the periodic table. This group of metals was chosen because it contains both paramagnetic and ferromagnetic elements as well as metals having positive and negative Hall coefficients. It is, therefore, possible to test whether the variations in the Hall effect in evaporated iron are due to its ferromagnetism or to the fact that its Hall effect is positive. If it is due to the latter, cobalt and iridium might be expected to have similar variations; if due to ferromagnetism, nickel, in spite of its negative Hall effect, and cobalt, might be expected to give results similar to iron.

On account of the difficulty of obtaining the metals in the proper form for evaporation, only iron, cobalt, nickel, palladium, platinum, iridium and rhodium were investigated. Of these, the last three and especially the last two were so difficult to evaporate[4,5,6,7] that only a few films were studied. The effect of heat treatment during and after deposition was investigated in some of the films. Films of nickel and cobalt were examined microscopically for crystal structure.

Experimental

The method of producing the evaporated films was the same as that used by Steinberg[1] with a few improvements in apparatus. Two microscope slides, one above and the other below the filament, were used for the deposition and by means of a heating element beneath the lower

[2] Weber and Oosterhuis, K. Akad. Amsterdam, Proc., **19**, 597 (1917).
[3] A. J. Sorensen, Phys. Rev. **24**, 658 (1924).
[4] J. H. I. Roberts, Phil. Mag. **25**, 271 (1913).
[5] W. Crookes, Roy. Soc. Proc., **A86**, 461 (1911).
[6] Harker and Kaye, Roy. Soc., Proc. **A88**, 522 (1913).
[7] Kaye and Ewen, Roy. Soc., Proc., **A89**, 58 (1913–14).

plate, a temperature difference could be maintained between the two allowing deposition of two films under differing temperature conditions. The approximate temperatures were measured by means of very fine copper-constantin thermocouples held in close contact with the plates.

The pressure in the tube during evaporation was in most cases 0.00075 mm of mercury or less as indicated by a McLeod gauge. In the later experiments, a mercury vapor trap was inserted between the pumps and the tube to eliminate the mercury vapor from the tube. At the pressure used, all parts of the plates were well within the mean free path of the gas in the tube.

The Hall effect, specific resistance and thickness were measured in the same manner and with the same apparatus as was used by Steinberg.[1] In measuring the Hall e.m.f. by the potentiometer method, the average of a number of readings was taken with the field in both directions.

The metals used were the purest that could be obtained in the proper form. Samples of the iron wire of Steinberg[1] and of Sorenson[3] were both used. One piece of nickel wire was obtained from Driver-Harris Company 98.5 percent pure. Another sample was the same as used by Sorensen. In neither the iron nor the nickel was any difference detected in the different samples. The cobalt films were made from cobalt deposited electrolytically on coils of tungsten wire to a depth of 0.25 mm. The differences in melting points and depth of layer probably kept the deposit tungsten-free. The palladium was furnished by Eimer and Amend as "pure." The platinum was Baker and Company's "special commercially pure" and was said to contain 99.5 percent of platinum. Flat strips of iridium and rhodium were produced by grinding down with carborundum wires about 0.7 mm in diameter obtained from the N. E. L. A. Research Laboratory.

Results

Hall effect and specific resistance. The values of the Hall coefficients and specific resistances for the evaporated films are shown in Table I in comparison with the values for bulk metals given by other observers. The Hall coefficient, R, is calculated from equation $R=E\epsilon/\beta I$ in which E is the Hall e.m.f., ϵ the thickness of the film, I the current in the film, and β the magnetic induction at right angles to the plane of the film and to the current. The specific resistance is designated by ρ and the subscripts, e and b, refer to evaporated and bulk metals, respectively. The values of R_e and ρ_e are the mean values for the number of films indicated deposited on places kept as cool as possible and at temperatures approximately the same. The thickness of the films ranged from 13 to

134$\mu\mu$ for iron, 11 to 166$\mu\mu$ for cobalt, 6 to 270$\mu\mu$ for nickel, 10 to 204$\mu\mu$ for palladium and 6 to 36$\mu\mu$ for platinum. Averaging R_e is justified since it is known to be a constant for all thicknesses for a given metal. In determining ρ_e, only those films were included which were thicker than the critical thickness. The values of R_b differ greatly for different observers and there is some question as to what values to use. Smith's[8] values for the first five metals were chosen because his paper also gives other data used.

TABLE I

The Hall coefficients and specific resistances for evaporated films and for bulk metals.

	Evaporated Metals					Bulk Metals			
	No. of	$R_e \times 10^3$(e.m.u.)		$\rho_e \times 10^6$(ohms)		$R_b \times 10^3$	$\rho_b \times 10^6$	$\frac{R_e}{R_b}$	$\frac{\rho_e}{\rho_b}$
Metal	films	Value	Mean dev.	Value	Mean dev.	(e.m.u.)	(ohms)[10]		
26Fe	14	+16	3	35	13	+11.0[8]	10	1.4	3.1
27Co	12	+29	5	216	63	+ 5.88[8]	9.7	4.9	23.0
28Ni	22	−99	13	200	58	−12.7[8]	7.8	7.8	25.0
46Pd	16	− 0.57	0.07	49	14	− 0.86[8]	11	0.66	4.4
78Pt	8	− 0.13	0.03	140	50	− 0.202[8]	10	0.64	14.0
77Ir	2	+ 0.034	0.002	66	5	+ 0.402[9]	6.1	....	10.8
45Rh	2	No effect	.....	57	3	No data	4.69	....	12.0

*Since iridium and rhodium films were not deposited within the mean free path, these results must not be considered as conclusive.

The Hall coefficients of the evaporated paramagnetic metals are smaller than in bulk as was found by Steinberg[1] for the diamagnetic metals, silver and copper; while for the ferromagnetic metals, these coefficients are larger than in bulk as was found by Steinberg for iron. It must be concluded that the increased Hall effect in evaporated films is a characteristic of ferromagnetism rather than of the sign of the Hall effect. These variations from bulk, being in opposite directions for different metals, practically eliminate the possibility that the observed results are due to an error in assuming the density of the films to be the same as in bulk.

Effects of heating. Heating films of iron, cobalt and nickel to a temperature of about 300°C during evaporation had the effect of reducing both R_e and ρ_e nearly to the values for the massive metals. For two films deposited at the same time and under the same conditions except for a temperature difference of about 100°C, both R_e and ρ_e were from 25 to 60 percent smaller for the heated film. The effect of heating after deposition was also investigated in nickel films with approximately the same results.

[8] A. W. Smith, Phys. Rev. **30**, 1 (1910).

[9] H. Zahn, Ann. d. Physik **16**, 148 (1905).

[10] Smithsonian Tables.

No effect of heating was observed in the non-ferromagnetic metals.

Saturation effects. It is known that with the ferromagnetic metals the equation $R=E\epsilon/\beta I$ fails to hold for the larger values of β and the Hall e.m.f. is said to become saturated. Steinberg[1] has shown that for evaporated iron this saturation occurs at a much lower value of β than for bulk iron. This result is confirmed only in a general way. Fig. 1 shows $E\epsilon/I$ plotted as a function of β for iron. Curves A, B, C and D, are for evaporated films and the other curve for bulk iron is taken from Smith's[8] paper. These curves show saturations at an induction only slightly less than

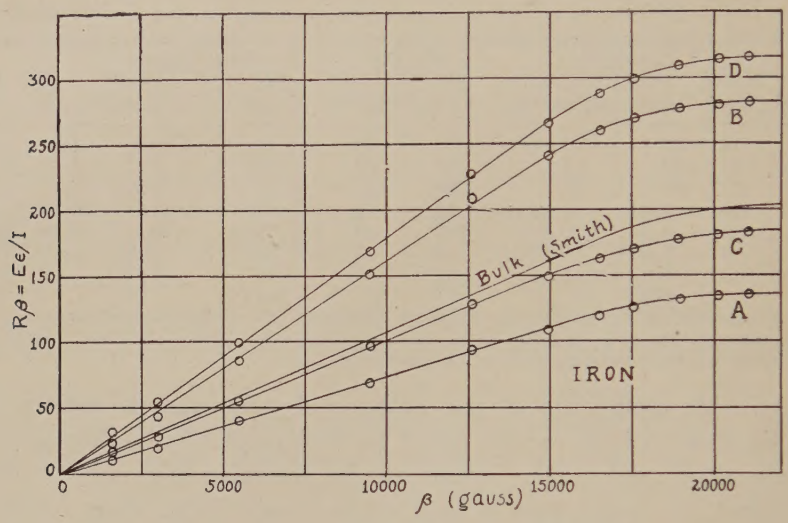

Fig. 1. Saturation of Hall e.m.f. and effect of heat treatment in evaporated iron. A and C are for films heated at a higher temperature.

for bulk metal. Similar curves for cobalt are given in Fig. 2 showing saturation at about 12,500 gauss as compared with 13,500 for bulk. Figs. 3 and 4 show corresponding curves for nickel. For the evaporated films, saturation occurs at about 2500 to 3000 and for bulk at about 6000.

These curves also show effects of heat treatment of the films which are evidenced in two ways. In the first place, the slopes of the curves give the values of the Hall coefficients, which have been shown to be larger for the less heated films. In Fig. 1, curves A and C are for iron films deposited on heated surfaces, B and D, on surfaces kept as cool as possible. Films A and B were deposited at the same time. Similar curves for cobalt are given in Fig. 2. Curves A and B are for films made at the same time, A being slightly more heated. C is for a film deposited on an especially hot surface, the definite temperature of which is not known. In the curves of Fig. 3 the pairs A,B and C,D are for nickel films made at

the same time, respectively, A and C being deposited at the higher temperatures. Fig. 4 shows effects of heating nickel films after deposition.

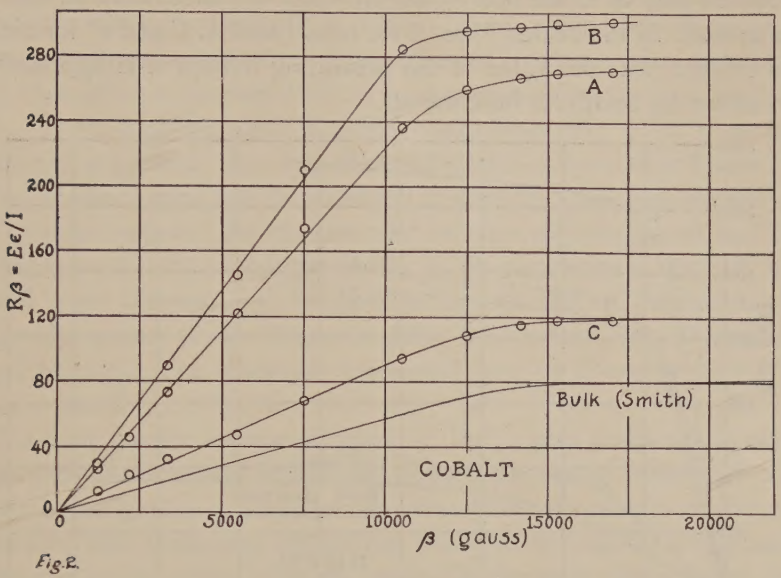

Fig. 2. Saturation of Hall e.m.f. and effect of heat treatment in evaporated cobalt. C is for a film heated at a higher temperature.

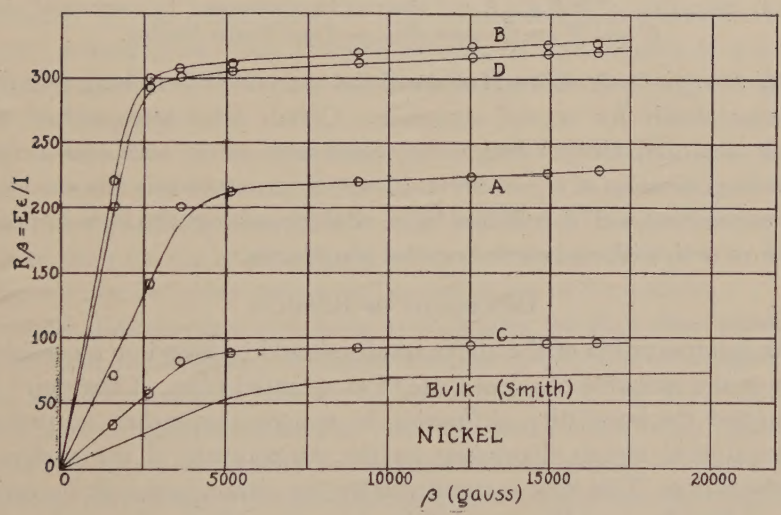

Fig. 3. Saturation of Hall e.m.f. and effect of heat treatment in evaporated nickel. A and C are for films heated at a higher temperature.

Curves E' and F' are for the same films as E and F, respectively, taken after heating F' to the softening point of glass and E' to approximately 100°C less.

The second effect of heating shown in these curves is a shift in the magnetic induction necessary to produce saturation. This effect is evidenced only in nickel and cobalt although the effect may be true for iron as well. In the heated films, C for cobalt and A, C and F' for nickel, it is evident that the value of the saturating induction is approaching that shown by Smith for bulk metals.

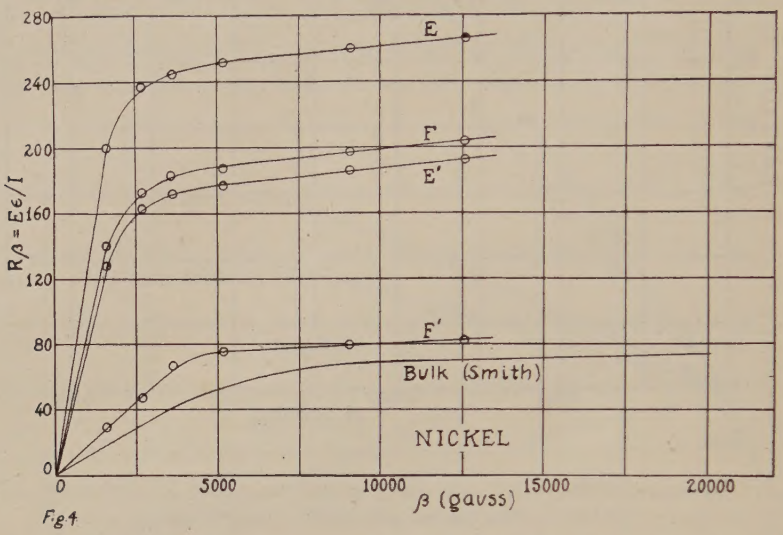

Fig. 4. Saturation of Hall e.m.f. and effect of heat treatment in evaporated nickel. E' and F' are the same films as E and F after heating.

Microscopic study. Several of the nickel and cobalt films were examined microscopically for crystal structure. Cobalt films were etched with picric acid and alcohol and nickel films with nitric acid and alcohol. At a magnification of about 300, evidence of structure was observed both by transmitted and by reflected light. Before etching, the films appeared quite smooth with no trace of crystal boundaries.

Discussion of Results

An interpretation of the above results should be based on a consideration of the probable physical state of evaporated films. Langmuir[11] has suggested the possibility of forming by evaporation either amorphous or crystalline metals depending on the temperature of the surface of condensation. This view is confirmed by the ultramicroscopic investigation of Reinders and Hamburger[12] in which they observed crystal growth in evaporated metal films in changing from liquid air temperature to

[11] I. Langmuir, Am. Chem. Soc., J38, 2221 (1916).

[12] Reinders and Hamburger, K. Akad. Amsterdam, Proc. **19**, 958 (1917); *ibid.* **20**, 1135 (1918).

room temperature. They were unable to obtain silver without crystalline structure but tungsten formed a deposit at the temperature of liquid air which could not be resolved. At room temperature, all of the films showed structure. Since the films of the present investigation were all deposited at temperatures considerably above room temperature, they were probably crystalline, a conclusion which is supported by microscopic examination. Three possible ways in which these films may differ from bulk metal are suggested. (1) The observed effects of heating indicate that the crystalline grains may be smaller; (2) since the films were not worked, the material between the crystals may be more porous and spongy, consisting possibly of amorphous metal or of very minute crystals with actual gaps between; (3) because of the method of deposition, the crystalline grains of the films may differ in structure from those of the metal in bulk. The observed results will now be discussed with these ideas in mind.

The high specific resistances found in the present study are in agreement with the results of Weber and Oosterhuis[2] and of Steinberg.[1] Also in the investigation of Reinders and Hamburger[12] referred to above, it was found that increasing crystal size was accompanied by a decrease of resistance which agrees with the results of the heat treatment of iron, cobalt and nickel. Thompson[13] has shown in an investigation on bulk iron that the resistance becomes smaller as the crystals are made larger by annealing. These results seem to lead to the conclusion that the high specific resistance in these evaporated films is due in part to smaller crystalline grains. The heating may also affect a difference in the material between the grains.

An explanation of the mechanism of resistance, which might come under the third possible difference listed above, is suggested by Höjendahl[14] who attempts to explain certain conduction phenomena on the basis of the rotation of the elliptic orbits of the valence electrons. This suggests a need of x-ray and optical investigation of these films.

Greater difficulty is encountered in explaining the Hall effect phenomena because the difference between the Hall coefficients for evaporated films and for metals in bulk are of opposite sign for the ferromagnetic and non-ferromagnetic elements. On the basis of the belief that the crystalline grains are smaller and in less intimate contact in the evaporated films than in bulk, the low Hall coefficients for the non-ferromagnetic metals may be quite well accounted for by assuming that only the crystalline grains contribute to the Hall effect, and that the measured

[13] F. C. Thompson, Phil. Mag. **31,** 357 (1916).
[14] K. Höjendahl, Phil. Mag. **48,** 349 (1924).

current through the film is carried to a larger extent by the gaps between the grains than in bulk, making the current through the crystalline grains themselves smaller than the measured value. Since $R=E\epsilon/\beta I$, using a current which is too large would have the effect of decreasing the value of R. With the exception of this error in the value of the current, one should expect the same R for the same material.[15] A further test of the effect of small crystalline grains might be made by thorough heat treatment of these films, if we may assume that high temperature promotes crystal growth.

In the ferromagnetic metals, the situation is evidently quite different, for, as has been shown, the Hall coefficients for evaporated films are considerably larger in absolute value than for the metals in bulk. If the above explanation is valid for the non-ferromagnetic metals, there must be a similar effect in iron, cobalt and nickel, which is hidden by a greater effect in the opposite direction. That this latter effect is closely related to ferromagnetism is evidenced by the fact that nickel, in spite of its negative Hall effect, behaves in a manner similar to iron and cobalt; however, it is difficult to conceive of a change in magnetic properties that would produce the greatest changes in nickel, the least ferromagnetic of the three. That there are differences in the magnetic properties of these films is seen from a consideration of Sorensen's[3] results, but no specific correlation with the present results is suggested.

It seems from the above considerations that there must be some fundamental change in the Hall effect in the separate crystalline grains to account for the observed results on iron, cobalt and nickel. An alteration of the atomic fields of force by some distortion of the crystalline grains or other asymmetry resulting from the conditions of deposition may offer a possible explanation.

The present results on the saturation of the Hall e.m.f. might seem to indicate a lack of proportionality between the Hall effect and the intensity of magnetization in iron, cobalt and nickel as found for these metals in bulk by DuBois[16] and Kundt.[17] This is not a necessary conclusion, however, since no magnetic measurements have been made on thin films magnetized normally to the plane as in Hall effect measurements. Inasmuch as H must be small, on account of the demagnetizing effect in a thin film, β is probably nearly equal to $4\pi I$, but the actual relation is unknown.

[15] G. W. Stewart, Phys. Rev. **17**, 232 (1921).
[16] H. G. J. DuBois, Ann. d. Physik **31**, 491 (1887).
[17] A. Kundt, Ann. d. Physik **49**, 257 (1893).

Smith's[8] results on the variation of the Hall effect with temperature should be noted. The Hall coefficients with increasing temperature increased for the ferromagnetic metals and decreased for the non-ferromagnetic metals. This is similar to the above results. Also, he observed a similar decrease in the value of the magnetic induction necessary to produce saturation of the Hall e.m.f. in the ferromagnetic metals.

The average values of the Hall coefficients for evaporated iron, cobalt and nickel are 1.4, 4.9 and 7.8 times, respectively, the values for the metals in bulk. The magnetic induction necessary to produce saturation of the Hall e.m.f. is for nickel about 60 percent lower than in bulk, for cobalt about 8 percent lower and for iron only slightly lower. These results seem significant when we consider that in both cases these variations are in the order of the atomic number of these elements and may indicate some fundamental relation to atomic structure. If the increase in the Hall effect is due to an asymmetry in the crystals, then there is a causal atomic change related to the increase in atomic number.

In conclusion, the writer wishes to express his appreciation to the members of the Department of Physics of the State University of Iowa for their assistance and interest, and especially to Professor G. W. Stewart under whose direction the work was carried on.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA.
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